

EXAFS Study of Cu(II) Adsorption on Calcite in The Presence of Humic Acid

Y.J. Lee, E.J. Elzinga, and R.J. Reeder (SUNY, Stony Brook)

Beamline(s): X18B

Introduction: Understanding and quantifying the molecular configuration of metal binding on mineral surfaces in the presence of natural organic matter (NOM), including humic acid (HA) or fulvic acid (FA), is fundamental to the development of predictive models for the uptake and retention behaviors of trace or toxic metals in natural ecosystems. To better understand mineral-metal-NOM interactions, the molecular configuration of Cu(II) sorbed on calcite exposed to humic acid (HA) was characterized using EXAFS spectroscopy.

Methods and Materials: The calcite sorbent used in this study had an N_2 -BET surface area of $10 \text{ m}^2 \text{ g}^{-1}$. Calcite-water suspensions of $0.5 \text{ g calcite L}^{-1}$ were equilibrated at atmospheric CO_2 pressure for 2 weeks, yielding an equilibrium pH of 8.3. For HA-calcite samples, the same procedure was used with Suwannee River HA (from The International Humic Substance Society (IHSS)). After aging calcite with HA, the supernatant was decanted and replaced by HA-free pre-equilibrated solution with calcite (no change of pH in solution). All suspensions were then spiked with appropriate aliquots of a 0.01 M CuCl_2 stock solution to achieve initial Cu concentrations of $5 \text{ } \mu\text{M}$. After reaction for 72 hr, the samples were filtered through $0.22 \text{ } \mu\text{m}$ filter paper to collect the wet calcite solids for EXAFS characterization. Room temperature scans were taken at the Cu K-edge, using a 13-element solid state detector. Data analysis was done with WinXAS2.0 [1], in combination with the FEFF7 code [2], following standard procedures.

Results: The Fourier transforms of the k^3 -weighted χ spectra of Cu(II)-calcite-HA adsorption samples are shown in Figure 1. EXAFS results showed scattering from four equatorial oxygens approximately located at $\sim 1.95 \text{ } \text{\AA}$ and Ca at $\sim 3.90 \text{ } \text{\AA}$. This observation indicates that Cu(II) forms mononuclear inner-sphere Jahn-Teller distorted adsorption complexes on the calcite surface. These distances are very similar to EXAFS results of Cu(II) sorbed onto calcite without humic acid (HA)[3]. On the basis of our EXAFS observations, we could not identify ternary complexes at the Ca sites calcite surface. These observations suggest that Cu(II) binding to our NOM-reacted calcite was not significantly influenced by direct binding to the NOM coating under our experimental conditions, but rather proceeds by inner-sphere coordination to CO_3 surface groups.

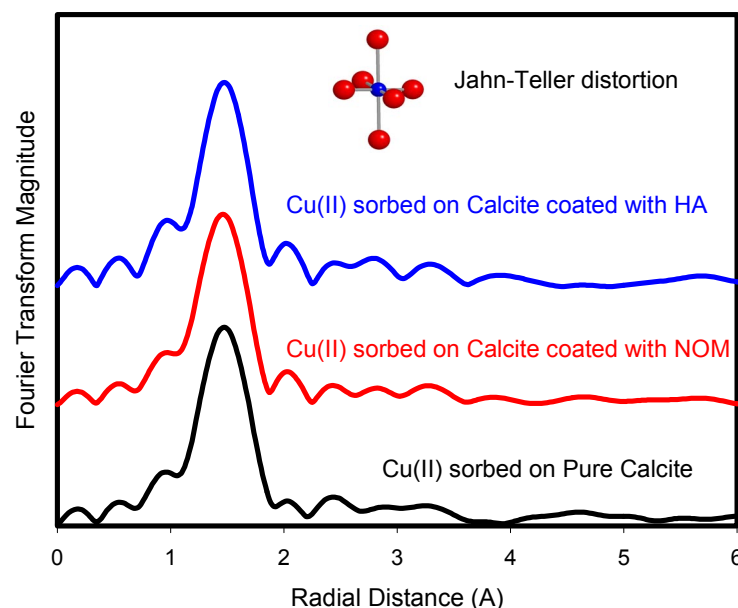
References:[1] Ressler T. (1997) J. Physique IV, **7**, C2-269.[2] Zabinsky S.I., Rehr J.J., Ankudinov A., Albers R.C., and Eller M.J. (1995) Phys. Rev. B **52**, 2995-3009.[3] Elzinga and Reeder (2002) Geochim Cosmochim Acta **66**, 3943-3954.

Figure 1. Radial structure functions for Cu(II) sorbed on the calcite surface in the absence or presence of natural organic matter.